New operation strategy for driving the selectivity of NO$_x$ reduction to N$_2$, NH$_3$ or N$_2$O during lean/rich cycling of a lean NO$_x$ trap catalyst☆

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ABSTRACT

Periodical regeneration of NO$_x$ storage catalyst (also known as lean NO$_x$ trap) by short rich pulses of CO, H$_2$ and hydrocarbons is necessary for the reduction of nitrogen oxides adsorbed on the catalyst surface. Ideally, the stored NO$_x$ is converted into N$_2$, but N$_2$O and NH$_3$ by-products can be formed as well, particularly at low-intermediate temperatures. The N$_2$ and N$_2$O products are formed concurrently in two peaks. The primary peaks appear immediately after the rich-phase inception, and tail off with the breakthrough of the reductant front accompanied by NH$_3$ product. The secondary N$_2$ and N$_2$O peaks then appear at the rich-to-lean transition as a result of reactions between surface-deposited reductants/intermediates (CO, HC, NH$_3$, —NCO) and residual stored NO$_x$ under increasingly lean conditions.

Based on these mechanistic insights, we propose and demonstrate a novel strategy for driving the selectivity of the secondary peaks towards desired products. It is based on a transition phase of neutral or slightly lean (nearly stoichiometric) character inserted between the rich and the fully lean phase. This strategy allows more complete regeneration of the catalyst with higher N$_2$ yield and without the undesired formation of a secondary N$_2$O peak. Furthermore, NH$_3$ can be formed during this slightly lean transition phase without any CO or hydrocarbons breakthrough. Such ammonia formation is desirable in the exhaust gas aftertreatment systems combining LNT with passive SCR technology.

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1. Introduction

Lean NO$_x$ trap (LNT) catalysts represent a major element in combined systems used for the aftertreatment of exhaust gas from automotive lean gasoline and diesel engines. It enables NO$_x$ adsorption under lean conditions when an excess of oxygen impedes efficient NO$_x$ reduction. NO$_x$ adsorption processes are relatively slow and quite well understood [1–5]. However, because NO$_x$ storage capacity of the LNT is limited, the catalyst needs to be regenerated periodically by rich pulses containing an excess of reductants (CO, H$_2$ and hydrocarbons) from fuel. The regeneration products generally include N$_2$ (desired final product), NO$_x$ (desorbed), NH$_3$ and N$_2$O. The mechanisms of highly dynamic reduction of stored NO$_x$ during and immediately after the regeneration pulse have not yet been entirely clarified, particularly with respect to the processes taking place immediately after rich pulse completion.

Recent research has shown that local NO$_x$ reduction selectivity towards individual N-products is determined by the ratio between the rate of NO$_x$ release and that of Pt group metal (PGM) reduction which depends on the individual "light-off" characteristics of different reductants (CO, H$_2$, hydrocarbons). Thus, the selectivity can be controlled by gas composition, temperature and the length of the rich pulse. During and after catalyst regeneration, N$_2$ and N$_2$O products are formed concurrently in two peaks. While the primary peaks are associated with rich pulse inception and appear at the catalyst outlet during regeneration, the secondary peaks can be observed immediately after the rich pulse as a result of subsequent reactions [6–13]. The secondary peak diminishes with a longer and more complete regeneration that does not leave enough residual NO$_x$ and reduction intermediates on the catalyst surface [14].

As the reduction front travels along the monolith channel during the rich phase, the reductants can react with the stored NO_x, either at the leading edge of the reduction front over incompletely reduced PGM sites, which typically leads to N_2O formation, or behind the front in the fully reduced part of the catalyst resulting in N_2 and NH_3 production. After switching back to lean conditions, the adsorbed reductants and reduction intermediates can further react with the residual NO_x remaining on the surface due to an incomplete regeneration and form additional N-products [11,14]. These secondary products can significantly contribute to the overall N_2 and N_2O yield [6,7].

During regeneration using H_2 as a reducing agent, NH_3 is the main product of NO_x reduction. It is formed in the front part of the catalyst and transported by convection into the still oxidized downstream zone where it reacts with stored oxygen and NO_x to produce N_2 and N_2O. This leads to a delayed breakthrough of NH_3 at the reactor outlet [12,13].

In the case of reduction with CO, reduction of stored NO_x can proceed through an isocyanate (−NCO) surface intermediate [15–18] that can react with NO, O_2, stored nitrites/nitrates and H_2O to form N_2O, N_2 or NH_3. Ammonia formed by hydrolysis of −NCO can further react with NO_x stored on the catalyst surface and thus contribute to the overall NO_x conversion [19].

When hydrocarbons are used for NO_x reduction, a wide variety of organic species can be produced during LNT regeneration and contribute to both primary and secondary N_2O formation [20]. Parallel indirect pathways of NO_x reduction by CO and hydrocarbons involves water gas shift and steam reforming reactions where hydrogen formed from CO and hydrocarbons in the presence of water acts as the NO_x reducing agent [10,21].

Although tailpipe ammonia slip is generally undesired, NH_3 is a reactive by-product that can be used for further NO_x reduction; for example, in the case of combined NO_x storage and NH_3-SCR catalytic systems [22,23]. In contrast, N_2O is an undesired by-product with low reactivity; although not toxic, it possesses a high global warming potential. Once N_2O is created, it is transported downstream remaining unchanged because it is difficult to decompose under real driving conditions. Therefore, reducing the amount of produced N_2O is an important challenge for LNT catalyst operation control.

In this paper we focus on selectivity of the products formed in the secondary peak at rich-to-lean transition. Although up to 50% of the total N_2O product can originate from the secondary peak [6], no suggestions have yet been published for specifically addressing this issue. Our previous research [6,9,11,14] enabled better understanding of the general principle of NO_x reduction selectivity depending on the actual oxidation state of PGM sites. Particularly, we have shown that N_2O formation is minimized over well reduced PGM sites, regardless of the specific reductant used [11]. We also proved experimentally that the secondary peaks originate from the reactions between residual stored NO_x and adsorbed reduction intermediates remaining on the catalyst surface when switching back to lean phase, and their selectivity is insensitive to the presence of NO_x in the gas phase [14]. Finally, we demonstrated that the secondary peaks diminish with a longer rich phase and more complete regeneration that leave less residual NO_x and/or reduction intermediates on the catalyst surface [6,14].

Our findings enabled us to formulate a novel LNT operation strategy introduced in this paper. It aims to minimize secondary N_2O formation and to better utilize available reductants. The strategy is based on a transition phase, of neutral or slightly lean (nearly stoichiometric) character, inserted between the rich and fully lean phases. During this transition phase, the adsorbed reductants/intermediates and residual stored NO_x remaining on the surface continue to react over well reduced PGM sites even beyond the rich regeneration phase, thereby preventing secondary

Table 1
Inlet gas composition used in the first set of experiments.

Component	Concentration		
	Lean	Rich	Transition
Nitrogen oxide (NO)	300 ppm	300 ppm	300 ppm
Oxygen (O_2)	10%	0%	0.32%
Carbon monoxide (CO)	0%	0/3.4%	0.5%
Propene (C_3H_6)	0 ppm	3780/0 ppm	556 ppm
Water (H_2O)	5%	5%	5%
Carbon dioxide (CO_2)	0%	0%	0%

N_2O formation and shifting selectivity towards the desired N_2 product. This strategy also enables additional NH_3 formation without any CO or hydrocarbons breakthrough, which is highly desirable for the coupled LNT-SCR applications.

2. Experimental

For the experiments, a fully formulated commercial LNT catalyst, containing platinum group metals (Pt, Pd, Rh) together with Ba, CeZr, MgAl and Al oxides, was used. This particular LNT (lean-GDI, BMW 120i, model year 2009) serves as a reference catalyst within the CLEERS research community [24]. Two different types of samples were studied in slightly different set-ups; a cylindrical sample and rectangular slice samples. The two types of samples were cut from the same monolith. Due to spatial variation of washcoat loading in the monolith, the NO_x storage capacity and catalytic activity of the two sets of samples differed to a certain extent. However, the same trends were observed for both samples and experimental set-ups.

In both cases, a bench flow reactor was used to study the dynamics of products evolution. The desired gas mixture composition was defined by mass flow controllers (MFCs) and the prepared gas was pre-heated before entering the reactor. Synthetic gases were used to perform a set of cycling experiments. A rapid switching 4-way valve was used to alternate between individual gas mixtures that were prepared independently in two lines [6,9,14]. The gas hourly space velocity (GHSV) was 30,000 h^{-1} and the experiments focused on the temperature range 200–250 °C where the contribution of secondary N_2O and N_2 peaks is most significant. Several different lengths of the lean, rich and transition phases were used to reveal the NO_x reduction selectivity dependence on the gas mixture composition. The evolution of products at the reactor outlet was analyzed by a high-speed FTIR gas analyzer (MKS 2030HS). The outlet gas from the reactor was diluted 1:1 in order to achieve higher flow rate through the FTIR analyzer and so minimize the measured signal dispersion. The composition of examined gas mixtures for two sets of experiments is described in Tables 1 and 2.

The first experimental set was performed in a nearly isothermal steel lab reactor containing three identical rectangular samples of the catalyst in series (each 30 mm long, 5.7 mm in height, 29 mm in width). Evaporated water was admixed to the gas stream using Controlled Evaporation Mixer (CEM, Bronkhorst). Relatively low concentrations of reductants and oxygen were used (Table 1) during the nearly stoichiometric transition phase so that strong

Table 2
Inlet gas composition used in the second set of experiments.

Component	Concentration		
	Lean	Rich	Transition
Nitrogen oxide (NO)	300 ppm	300 ppm	300 ppm
Oxygen (O_2)	10%	0%	0.03%
Carbon monoxide (CO)	0%	3.4%	0%
Water (H_2O)	5%	5%	5%
Carbon dioxide (CO_2)	0%	0%	0%

Table 3
Timing for individual cycling experiments.

Cycling	Phase length			Composition
	Lean	Rich	Transition	
Classical Lean/Rich	60 s	5 s	–	Table 1 or 2
Lean/Rich/Transition #1	60 s	5 s	5 s	Table 1
Lean/Rich/Transition #2	60 s	5 s	30 s	Table 1
Lean/Rich/Transition #3	55 s	5 s	5 s	Table 2

exothermic effects were avoided. The gas was analyzed only by FTIR, so no information about the N_2 signal was available.

For the second set of experiments, a cylindrical catalyst sample (2.1 cm in diameter, 3.8 cm long) was used in a nearly adiabatic lab reactor. The catalyst sample was wrapped in Zetex insulation tape and inserted into a horizontal quartz glass tube reactor, which was heated by an electric furnace. Water was introduced by a high pressure liquid metering pump (Eldex) to a heated zone, vaporized instantly and added to the simulated exhaust mixture. The composition of the gas mixtures is displayed in Table 2. The composition of the lean and rich phases is exactly the same as in the first set of experiments. However, no reducing agent was present during the transition phase in the second set of experiments, where the slightly lean character was ensured by low oxygen concentration alone. In addition to FTIR, this experimental set-up also included a mass spectrometer to analyze the nitrogen product. The detailed analysis of products was enabled by the use of Ar carrier gas and isotopically labeled ^{15}NO [6]. Furthermore, CO_2 was excluded from the feed in all experiments to simplify the quantitative analysis of MS signals. It was previously demonstrated that the absence of CO_2 in the feed does not change the nature of the studied processes during LNT regeneration [6,14]; it only increases the effective NO_x storage capacity during the lean phase due to absence of competing carbonates on the adsorption sites [14].

The newly proposed operating strategy is based on the modification of traditional lean/rich cycling experiments by inserting a transition phase (slightly lean mixture) between the rich and lean phases to move the NO_x reduction selectivity towards the desired products. These modified cycling experiments were compared with the classical ones. All results were taken during stabilized cycling. The timing options used in this study are listed in Table 3.

3. Results and discussion

To evaluate the effectiveness of the proposed strategy for typical operating conditions of an LNT catalyst, a transition phase with nearly stoichiometric composition was inserted between the fully rich and fully lean phases and these results were then compared with classical lean/rich cycling results.

Typical reactant profiles during stabilized cycling experiments at 250 °C with C_3H_6 reductant can be seen in Fig. 1, where each figure covers the end of a lean phase (55–60 s), the whole regeneration (60–65 s) and a transition phase (65–70 s in Fig. 1b) followed by the beginning of a subsequent lean phase. Comparing Fig. 1a and b shows that the transition phase significantly reduces the secondary N_2O peak; the transition phase allows the residual stored NO_x and adsorbed reductants/surface-intermediates to react over a relatively well-reduced catalyst surface, which results in lower N_2O and correspondingly greater N_2 and NH_3 production. In contrast, without the transition region, these residual surface species would react over a more oxidized catalyst surface which would shift the selectivity to N_2O (Fig. 1a).

The modified Lean/Rich/Transition #1 cycle (60/5/5 s) is 5 s longer than classical 60/5 s lean/rich cycle. The transition phase makes the regeneration more effective, even though the transition phase is slightly lean. This is demonstrated in Fig. 1b by the
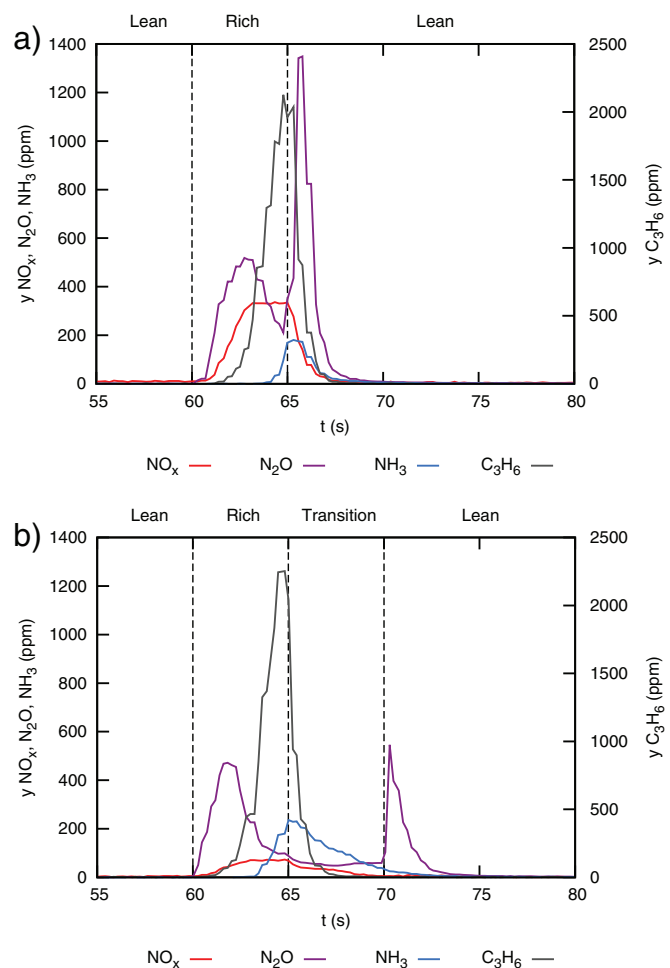

Fig. 1. Evolution of NO_x, NH_3, N_2O and C_3H_6 concentration during and after the catalyst regeneration by C_3H_6 at 250 °C for (a) Lean/Rich 60/5 s cycling and (b) Lean/Rich/Transition #1 60/5/5 s cycling (Table 1).

decreased rich-phase NO_x release and no measurable NO_x breakthrough at the end of the lean phase (60 s) compared to classical cycling (Fig. 1a); i.e., there is lower overall stored NO_x on the catalyst with the transition phase included. The slightly different shape of the primary peaks is also a result of more effective regeneration in the case when transition phase is used.

In comparison with the fully lean regime, somewhat higher fuel consumption is associated with the slightly lean transition phase. However, this fuel penalty is significantly lower than the penalty during rich phase. Considering the additional NO_x reduction achieved during the transition phase, it is possible to apply a shorter rich phase followed by the transition phase and still achieve the same NO_x conversion as with a longer rich phase during the conventional lean/rich cycling. It can be therefore expected that properly optimized lean/rich/transition operation will not substantially increase fuel consumption over the level of conventional lean/rich cycling.

Even more significant effect on N_2O reduction can be observed in Fig. 2, where CO is used as a reductant at 200 °C (around CO light-off temperature). More effective regeneration during Lean/Rich/Transition #1 cycling leaves less NO_x on the catalyst surface which in turn results in the earlier breakthrough of unreacted CO during the rich phase (Fig. 2b); this indicates that complete NO_x reduction is achieved with less CO consumed. This is enabled by the continuing reactions of the adsorbed reductants and intermediates during the transition phase; for example, –NCO reactions with
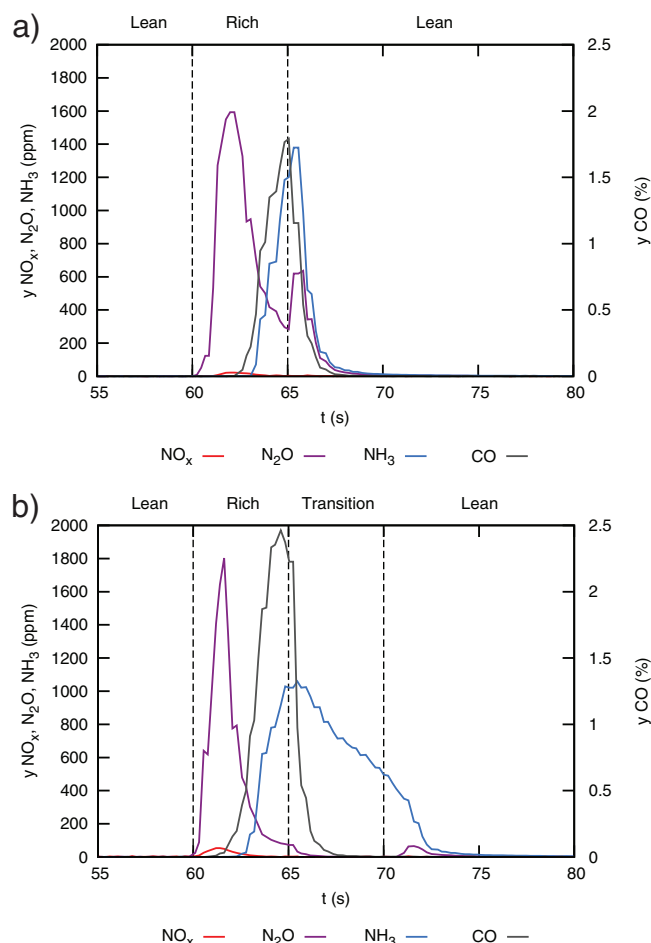
Fig. 2. Evolution of NO_x, NH_3, N_2O and CO concentration during and after the catalyst regeneration by CO at 200 °C for (a) Lean/Rich 60/5 s cycling and (b) Lean/Rich/Transition #1 60/5/5 s cycling (Table 1).

residual stored NO_x yielding N_2 as well as $-NCO$ hydrolysis to NH_3. Continuing NH_3 formation during the slightly lean transition phase is clearly visible (Fig. 2b). In the absence of the transition phase (Fig. 2a), the majority of adsorbed reductants and intermediates is quickly oxidized under excess-oxygen conditions so that the NO_x-reducing potential of these surface-accumulated species is wasted. In this case, the continuing reactions between residual stored NO_x and adsorbed reductants/intermediates take place under highly oxidizing conditions causing production of a significant N_2O peak.

Thorough catalyst regeneration with almost complete elimination of secondary N_2O generation can be seen in the case of a prolonged transition phase (Fig. 3). This demonstrates that a longer transition phase can limit the amount of secondary N_2O to almost zero, which is similar to the results obtained with very long rich regeneration [6,14]. The common aspect of these two solutions for eliminating secondary N_2O is that the residual surface NO_x and reduction intermediates are allowed to react under overall reduced surface conditions for an extended period. As a result, more complete regeneration is achieved, and the correspondingly lower final concentrations of residual surface NO_x and intermediates minimize the potential for N_2O formation at the transition to fully lean, oxidizing conditions. The main advantage of the proposed transition phase resides in the fact that more complete regeneration and lower secondary N_2O formation is achieved without the undesired reductant breakthrough that occurs during a long rich phase [10].

The calculated NO_x conversions together with N_2O, NH_3 and N_2 yields are shown in Fig. 4. Using the new strategy with the added
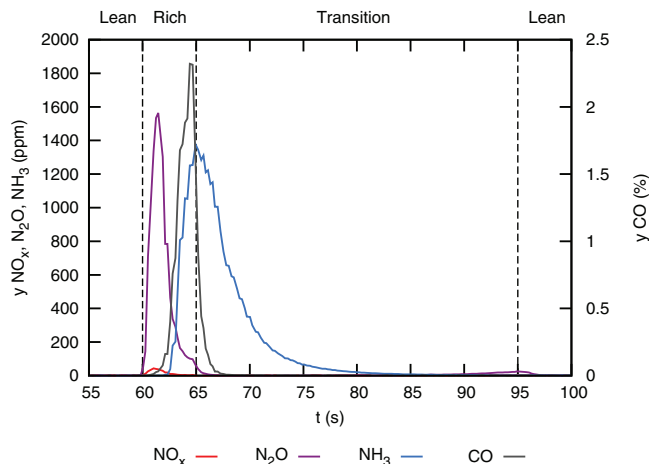

Fig. 3. Evolution of NO_x, NH_3, N_2O and CO concentration during and after the catalyst regeneration by CO at 200 °C for the Lean/Rich/Transition #2 60/5/30 s cycling (Table 1).

transition phase, we achieved 31% reduction in total N_2O emissions in the case of regeneration by CO at 200 °C. When C_3H_6 was used as a reductant at 250 °C, 33% reduction of total N_2O emissions and a noticeable improvement in NO_x conversion was observed. No increase in NO_x conversion is visible for CO at 200 °C because
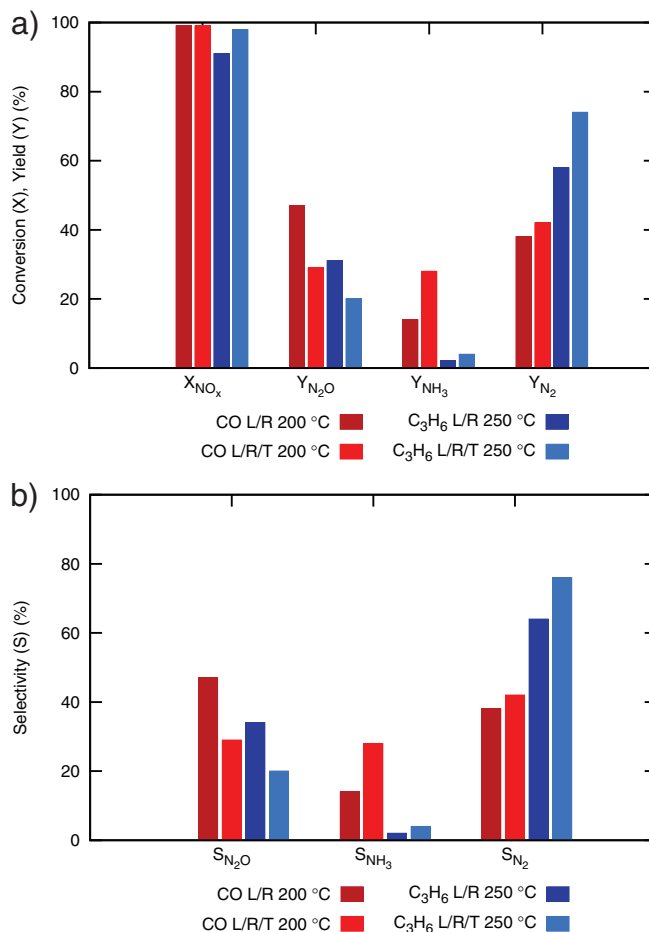

Fig. 4. Integral NO_x conversion together with (a) NH_3, N_2O and N_2 yield and (b) selectivity towards NH_3, N_2O and N_2 during Lean/Rich (60/5 s) and Lean/Rich/Transition #1 (60/5/5 s) cycling; regeneration by CO at 200 °C or by C_3H_6 at 250 °C (Table 1).
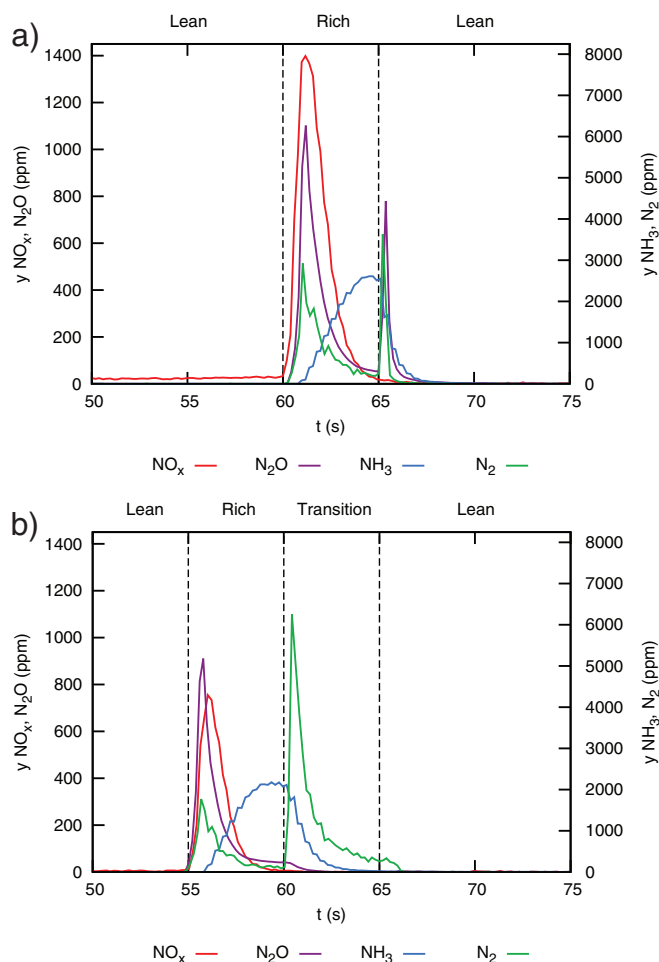
Fig. 5. Evolution of NO_x, NH_3, N_2O and N_2 concentration during and after the catalyst regeneration by CO at 250 °C for (a) Lean/Rich 60/5 s cycling and (b) Lean/Rich/Transition #3 55/5/5 s cycling (Table 2).

Fig. 6. Integral NO_x conversion together with (a) NH_3, N_2O and N_2 yield and (b) selectivity towards NH_3, N_2O and N_2 during Lean/Rich (60/5 s) and Lean/Rich/Transition #3 (55/5/5 s) cycling (no reductants in the transition phase); regeneration by CO at 250 °C (Table 2).

the NO_x conversion during conventional lean/rich cycling was almost complete. Nevertheless, the production of N_2O decreased and N_2 and NH_3 increased in all studied cases when applying the lean/rich/transition cycling strategy. This clearly demonstrates that the transition phase enabled more effective utilization of the reductant injected during rich phase.

To further prove the benefits of the transition phase and to elucidate the underlying reaction mechanisms, a second set of experiments was performed eliminating reductants from the transition-phase gas mixture (Table 2). The experimental set-up was adapted in order to allow accurate detection of N_2 signal by a mass spectrometer, as described in Section 2. Eliminating transition-phase reductants made it possible to discriminate between the sources of reductive species during the transition phase reactions; i.e., in this case only the adsorbed reductants or intermediates from the preceding rich phase were available.

Fig. 5 illustrates the situation when CO was used as a reductant at 250 °C during the rich phase and no reductant was present in the transition-phase feed. The primary insight from these experiments was that inclusion of reductant in the transition-phase gas composition is not required to eliminate the secondary N_2O peak. This specifically demonstrates that the residual stored NO_x and adsorbed reductants/intermediates react together. The transition-phase gas composition influences these reactions only to the extent that it controls the surface redox state, or more specifically, the rate of transition from the reduced to the oxidized state. In the case of just slight oxygen excess, the oxidizing-front progression is
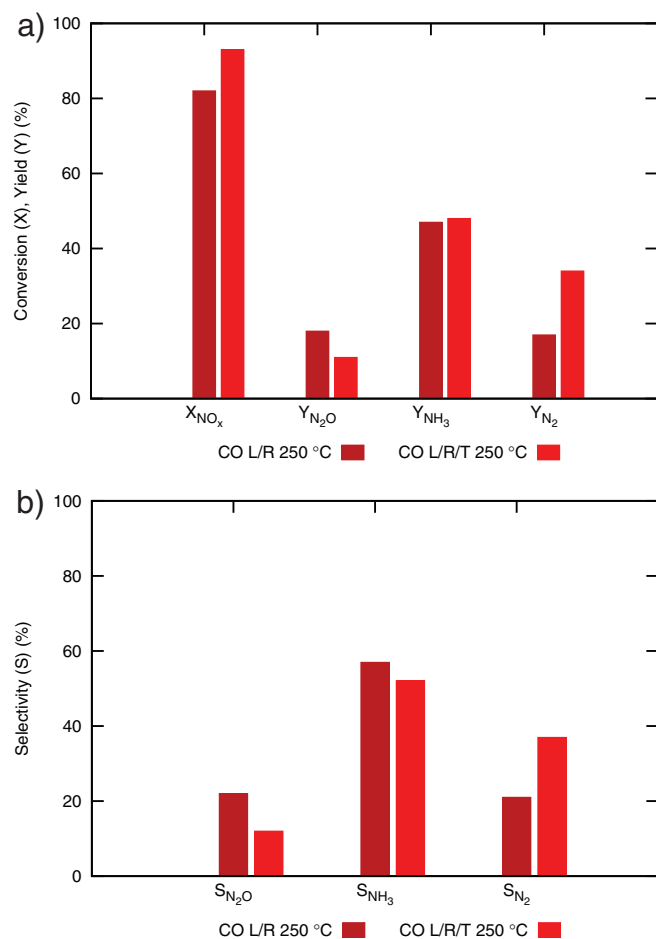
quite slow so that the reactions of surface-accumulated species can proceed over well reduced catalyst surface for an extended period. This observation further supports the general mechanism for NO_x reduction selectivity that we have proposed [6,11,14]. As with the previous experiments, the transition phase in Fig. 5b increased the regeneration efficiency, reducing the overall surface NO_x, resulting in lower NO_x breakthrough and eliminated secondary N_2O peak. Note that the primary N_2O peak decreased as well; this was caused by a lower concentration of stored NO_x at the end of the lean phase, resulting from more efficient regeneration in the previous cycle including the transition phase.

Less transition-phase NH_3 is formed at the higher temperature in Fig. 5b compared to Fig. 2b. This may suggest that at higher temperature, the oxidation of surface isocyanates to N_2 starts to dominate over slower hydrolysis to NH_3. Fig. 6 shows the calculated NO_x conversions together with N_2O, NH_3 and N_2 yields for these experiments. NO_x conversion and N_2 yield increased considerably when the transition phase was applied and 37% reduction of the total formed N_2O was observed. The measured dynamics of N_2 formation (Fig. 5) reveals that nitrogen production remarkably increases during the transition phase. In fact, the majority of N_2 is formed not during the rich phase but in the transition phase (Fig. 5b). Without the transition phase (Fig. 5a), the secondary N_2 peak is much smaller and at the same time a significant N_2O peak appears. This clearly shows that a larger portion of NO_x was converted to N_2 rather than to N_2O, when lean/rich/transition cycling was applied. This further supports the general mechanism

of NO_x reduction selectivity depending on the actual redox state of the catalyst surface [6,9,11,14]. The presented results collectively provide strong evidence for the advisability of the newly developed lean/rich/transition cycling strategy for LNT catalyst operation.

4. Conclusions

Our results show that introducing a slightly lean (nearly stoichiometric) mixture immediately after the regeneration phase may be beneficial to reducing N_2O emissions and improving the overall NO_x conversion under typical operating conditions of an LNT catalyst. This transition phase enables adsorbed reductants and intermediates to react further with the residual stored NO_x over a well reduced catalyst surface, which leads to additional NO_x reduction as well as shift in NO_x reduction selectivity from N_2O towards the desired products (N_2 and NH_3). Up to 37% reduction in N_2O emissions was demonstrated. Thus, the lean/rich/transition cycling appears to be a promising operating strategy for LNT catalyst control. The nearly stoichiometric transition phase can be easily achieved with lean gasoline engines and also with diesel when using proper control. Furthermore, this strategy provides an opportunity for additional NH_3 formation after the rich phase without any reductant breakthrough. Such NH_3 formation is highly desirable for coupled LNT-SCR applications.

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